TITLE OF THE INVENTION

FILM FORMING METHOD, SEMICONDUCTOR DEVICE AND SEMICONDUCTOR DEVICE MANUFCATURING METHOD

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a film forming method, a semiconductor device and a semiconductor device manufacturing method and, more particularly, a film forming method, a semiconductor device and a semiconductor device manufacturing method for ~~forming~~ covering wiring wi an interlayer insulating film having a low dielectric constant to cover a wiring.

2. Description of the Prior Art

In recent years, the miniaturization and the reduction in thickness of the pattern have been are required with for a the higher integration degree of and the higher density of ~~the~~ semiconductor integrated circuit devices, as well as for In ~~addition, since the~~ higher speed of the data transfer rate is also required.

Therefore, a the insulating film having a the low dielectric constant (referred to as a "low dielectric constant insulating film" hereinafter) and the small RC delay is employed. As Such insulating films, include there are the SiOF films having a the relative dielectric constant of 3.5 to 3.8, the porous SiO_2 films having ~~the~~ a relative dielectric constant 3.0 to 3.1, etc., for example.

However, such a essentially the low dielectric constant insulating film takes up and passes is ready to contain the moisture, and is ready to pass the incoming moisture. Therefore, if such a low dielectric constant insulating film is employed alone as the interlayer insulating film, the corrosion of the wiring and the increase in the leakage current are easily result caused. In order to prevent same to them, a ~~the~~ barrier insulating film containing Si and N or Si and C is often interposed between the wiring and the low dielectric constant insulating film.

More particularly, in a the semiconductor device having the multi-layered wiring, an the interlayer insulating film including containing barrier layers is formed between the upper wiring and the lower wiring. The interlayer insulating film containing barrier layers is formed by laminating a ~~the~~ barrier insulating film containing Si and N or Si and C, a ~~the~~ low dielectric constant insulating film, and a ~~the~~ barrier insulating film containing Si and N or Si and C, in sequence.

However, the insulating film containing Si and N has a ~~the~~ high relative dielectric constant. Therefore, even if such an insulating film is made ~~of the~~ thinner and ~~film thickness~~ ~~is~~ employed as the barrier insulating film, the dielectric constant of the overall interlayer insulating film is increased.

Also, the relative dielectric constant of the barrier insulating film containing Si and C is relatively

low, i.e. ~~such as~~ about 5, as compared to a ~~rather than the~~ barrier insulating film containing Si and N. But such a barrier insulating film containing Si and C cannot sufficiently suppress ~~the increase in the~~ leakage current.

SUMMARY OF THE INVENTION

It is an object of the present invention to ~~provide a film forming method, a semiconductor device and a semiconductor device manufacturing method, that are capable of lowering a~~ to lower the dielectric constant of an interlayer insulating film as a whole and to suppress~~ing~~ ~~a~~ change ~~of~~ in the dielectric constant due to moisture absorption, while preventing corrosion of ~~a~~ wiring and an increase in ~~a~~ leakage current.

In the film forming method according to the present invention, the silicon-containing insulating film is formed by ~~plasmanizing~~ converting to a plasma a film forming gas ~~consisting of~~ ~~any one~~ selected from ~~a~~ the group consisting of alkoxy compounds having Si-H bonds and siloxane compounds having Si-H bonds and ~~any one~~ an oxygen-containing gas selected from ~~a~~ the group consisting of O_2, N_2O, NO_2, CO, CO_2, and H_2O, and reacting the plasma components ~~to react~~. ~~According to the experiment,~~ It ~~is~~ has been found that ~~such~~ the resulting silicon-containing insulating film is dense, has ~~the~~ high moisture ~~proof~~ resistance, has ~~the small amount of contained~~ a low moisture ~~in the film~~ content, and has a ~~the~~ small relative dielectric constant.

Therefore, if the above silicon containing

insulating film is employed as the barrier insulating films (a lower protection layer and an upper protection layer) that constitute the interlayer insulating film interposed between the upper wiring and the lower wiring, and sandwich the low dielectric constant insulating film, the dielectric constant of the overall interlayer insulating film can be lowered while preventing ~~the~~ corrosion of the wiring and ~~the~~ increase in the leakage current.

~~According to~~ The semiconductor device of the present invention~~, the~~ includes a silicon-containing insulating film whose peak ~~of the~~ absorption intensity ~~of the~~ infrared ray~~s~~ is in a range of ~~the~~ wave number of 2270 to 2350 cm^{-1}, whose film density is in a range of 2.25 to 2.40 g/cm^3, and whose relative dielectric constant is in a range of 3.3 to 4.3, ~~is~~ formed on ~~the~~ a substrate.

~~According to the experiment of the inventors of this application, it is~~ It has been experimentally found that the silicon-containing insulating film having such characteristics has ~~the~~ high mechanical strength, is dense, is excellent in ~~the~~ water resistance, and has ~~the small~~ a low amount of contained moisture~~, in the film~~ like the silicon nitride film, and has ~~the~~ a relative dielectric constant smaller than ~~the~~ that of a silicon nitride film.

~~According to the configuration obtained by applying the silicon~~ In the manufacture of a silicon-containing ~~insulating film of the present invention to the~~ semiconductor device, the above

silicon- containing insulating film is formed to contact and cover the wiring ~~and contact to it, otherwise the above silicon-containing insulating film~~ or is formed as ~~the~~ a protection layer on ~~the~~ an insulating film that covers the wiring.

The silicon-containing insulating film of the present invention has ~~the~~ a low dielectric constant, ~~has the small amount of~~ contain~~ed~~s a low amount of moisture ~~in the film~~, is dense, and ~~is~~ has excellent ~~in the~~ water resistance. Therefore, if ~~the~~ a silicon-containing insulating film is employed as ~~the~~ a protection layer ~~for~~ covering the wiring~~s~~, etc., ~~the~~ corrosion of the wiring can be prevented by preventing ~~the incoming~~ moisture from entering the semiconductor device while reducing the parasitic capacitance between the wirings.

~~Also,~~ The upper and lower wirings and the interlayer insulating film interposed between the upper and lower wirings are provided on ~~the~~ a substrate, and the interlayer insulating film is formed of the silicon-containing insulating film according to the present invention.

~~Also,~~ The interlayer insulating film ~~is constructed~~ includes, in order from the bottom, ~~by the~~ a lower protection layer formed of the silicon-containing insulating film according to the present invention, the main insulating film, and ~~the~~ an upper protection layer formed of the silicon-containing insulating film according to the present invention.

If the main insulating film is ~~formed of the~~ a SiOF film, the silicon-containing insulating film according to the present invention can prevent the fluorine (F) ~~element~~ from diffusing to the outer peripheral portions of the silicon-containing insulating film. ~~Also, i~~ If the main insulating film is ~~formed of the~~ a porous insulating film having ~~the~~ high hygroscopicity, the silicon-containing insulating film according to the present invention can prevent the ~~incoming~~ ingress of ~~the~~ moisture into the porous insulating film and thus ~~the~~ prevent increase ~~of~~ in the dielectric constant due to ~~the~~ moisture absorption. ~~can be prevented.~~

Also, since ~~the~~ a silicon nitride film is not employed as the upper and lower protection layers ~~of~~ for the main insulating film, ~~but~~ and the silicon-containing insulating film having ~~the~~ a low relative dielectric constant is employed instead, the dielectric constant of the overall interlayer insulating film can be reduced.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG.1 is a side view ~~showing a configuration~~ of the plasma CVD film forming equipment employed in ~~a~~ the film forming method according to a first embodiment of the present invention;

FIG.2A to FIG.2E are sectional views showing structures of samples ~~employed to~~ examined to determine characteristics of a silicon-containing insulating film

that is formed by the film forming method according to the first embodiment of the present invention, and structures of comparative samples;

FIG.3A and FIG.3B are tables showing ~~examined results of a~~ film density of the insulating film that is formed by the film forming method according to a ~~the~~ second embodiment of the present invention using the sample of FIG.2A;

FIG.4 is a graph ~~showing examined results~~ of ~~a~~ moisture content and ~~a~~ water resistance of the silicon-containing insulating film that is formed by the film forming method according to the ~~a~~ second embodiment of the present invention using the sample of FIG.2A;

FIG.5A is a graph ~~showing examined results~~ of ~~an~~ infrared absorption intensity of the silicon-containing insulating film that is formed by the film forming method according to the ~~a~~ second embodiment of the present invention using the sample of FIG.2A;

FIG.5B is a graph ~~showing examined results~~ of ~~an~~ infrared absorption intensity of the silicon-containing insulating film that is formed by the film forming method according to the ~~a~~ second embodiment of the present invention using the comparative sample of FIG.2A;

FIG.6 is a graph ~~showing examined results~~ of ~~a~~ water resistance of the silicon-containing insulating film that is formed by the film forming method according to the ~~a~~ second embodiment of the present invention using the

sample of FIG.2B;

FIG.7 is a graph ~~showing examined results~~ of ~~a~~ water resistance as determined by ~~due to~~ a pressure-cooker test of the silicon-containing insulating film that is formed by the film forming method according to ~~a~~ the second embodiment of the present invention using the sample of FIG.2B;

FIG.8 is a table showing ~~examined results of an~~ adhesiveness ~~of~~ for the silicon-containing insulating film that is formed by the film forming method according to the second embodiment of the present invention, to a coated insulating film using the sample of FIG.2C;

FIG.9 is a graph ~~showing examined results~~ of ~~a~~ defect generating rate due to a heat cycle determined using the sample of FIG.2D according to the second embodiment of the present invention;

FIG.10 is a graph ~~showing examined results~~ of ~~a~~ copper barrier characteristic ~~to a copper~~ of the silicon-containing insulating film that is formed by the film forming method according to the second embodiment of the present invention;

FIGS.11A and 11B are sectional views showing a semiconductor device manufacturing method according to a third embodiment of the present invention;

FIGS.12A to 12C are sectional views showing a semiconductor device manufacturing method according to a fourth embodiment of the present invention;

FIGS.13A to 13F are sectional views showing a

semiconductor device manufacturing method according to a fifth embodiment of the present invention;

FIGS.14A to 14C are sectional views showing a semiconductor device manufacturing method according to a sixth embodiment of the present invention; and

FIG.15 is a sectional view showing a semiconductor device manufacturing method according to another ~~other~~ embodiment of the present invention.

DESCRIPTION OF THE PREFRRED EMBODIMENTS

Embodiments of the present invention will now be described ~~explained~~ with reference to the accompanying drawings hereinafter.

{First Embodiment}

FIG.1 shows ~~is a side view showing a configuration of the~~ parallel-plate type plasma CVD film forming equipment 101 employed in a film forming method ~~according to an embodiment of the present invention.~~

~~This plasma~~ CVD film forming equipment 101 as including ~~comprises~~ a film forming portion 101A wherein ~~that is the place at which~~ a silicon-containing insulating film is formed from a ~~by the~~ plasma ~~gas~~ on a substrate 20, and a film forming gas supplying portion 101B having a plurality of gas supply sources for ~~constituting~~ the film forming gas.

As shown in FIG.1, the film forming portion 101A has a chamber wherein ~~1 whose~~ pressure can be reduced, and ~~the~~ which ~~chamber 1~~ is connected to an exhaust~~ing~~ device 6 via an

exhaust pipe 4. A switching valve 5 for controlling the open ing and the closing communication close between the chamber 1, and the exhaust~~ing~~ device 6 is provided in the middle of the exhaust pipe 4. A pressure measuring means such as a vacuum gauge (not shown) for monitoring the pressure in the chamber 1 is provided in ~~to~~ the chamber 1.

~~A pair of opposing~~ An upper electrode (first electrode) 2 and a lower electrode (second electrode) 3 are provided opposing each other in ~~to~~ the chamber 1. A high frequency power supply (RF power supply) 7 for supplying ~~a~~ high frequency power at ~~having~~ a frequency of 13.56 MHz is connected to the upper electrode 2, while a low frequency power supply 8 for supplying a low frequency power at ~~having~~ a frequency of 380 kHz is connected to the lower electrode 3. The film forming gas is converted into a plasma ~~plasmanized~~ by supplying the power to the upper electrode 2 and the lower electrode 3 from these power supplies 7, 8. The upper electrode 2, the lower electrode 3, and the power supplies 7, 8 constitute the plasma generating means for converting ~~plasmanizing~~ the film forming gas into a plasma.

~~As~~ The plasma generating means may consist of ~~, there are the means for generating the plasma by~~ the first and second electrodes 2, 3 of the parallel-plate type, ~~the means for generating the plasma by ECR (~~Electron Cyclotron Resonance~~)~~ apparatus ~~method, the~~ means for generating ~~the~~ a helicon plasma by irradiation with ~~ing the~~ high frequency power from ~~the~~ an antenna, etc.~~, for example~~.

The upper electrode 2 is also used as a film forming gas distributor. A plurality of through holes are formed in the upper electrode 2, and ~~opening portions of~~ the through holes in the surface opposing ~~to~~ the lower electrode 3 serve as discharge ports for ~~(inlet ports) of~~ the film forming gas. The discharge ports of the film forming gas, etc. are connected to the film forming gas supplying portion 101B via a pipe 9a. Also, a heater (not shown) may be provided ~~to~~ in the upper electrode 2. ~~as the case may be. This is because,~~ If the upper electrode 2 is heated at ~~the~~ a temperature of almost 100 ℃ during the film formation, particles ~~made~~ of reaction products ~~of the film forming gas~~, etc. can be prevented from sticking onto the upper electrode 2.

The lower electrode 3 is also used as a loading table for the substrate 20. A heater 12 for heating the substrate 20 on the loading table is provided ~~to~~ in the lower electrode 3.

In the film forming gas supplying portion 101B, a supply source for the alkoxy compound having Si-H bonds; a supply source for the siloxane having Si-H bonds; a supply source for ~~anyone~~ an oxygen-containing gas selected from ~~a~~ the group consisting of oxygen (O_2), nitrogen monoxide (N_2O), nitrogen dioxide (NO_2), carbon monoxide (CO), carbon dioxide (CO_2), and water (H_2O); a supply source for the hydrogen (H_2); and a supply source for the nitrogen (N_2) are provided.

As for the alkoxy compound having Si-H bonds or the siloxane having Si-H bonds as the film forming gas to which the present invention is applied, the following~~s~~ ~~may be~~ are employed as ~~the~~ typical examples.

(i) alkoxy compound having Si-H bonds

trimethoxysilane (TMS: $SiH(OCH_3)_3$)

(ii) siloxane having Si-H bonds

tetramethyldisiloxane (TMDSO: $(CH_3)_2HSi\text{-}O\text{-}SiH(CH_3)_2$)

These gases are supplied appropriately to the chamber 1 of the film forming portion 101A via branch pipes 9b to 9f and a pipe 9a to which all branch pipes 9b to 9f are connected. Flow rate controlling means 11a to 11e and switching means 10b to 10k for controlling the opening and the closing of each of the branch pipes 9b to 9f are provided in the middle of the branch pipes 9b to 9f. A switching means 10a for controlling the opening and the closing of the pipe 9a is provided in the middle of the pipe 9a. Also, in order to purge the residual gas ~~in~~ from the branch pipes 9b to 9e ~~by flowing the~~ with N_2 gas, switching means 10l to 10n, 10p are provided for controlling the opening ~~and the~~ closing of communication between the branch pipe 9f, that is connected to the N_2 gas supply source, and remaining branch pipes 9b to 9e. ~~are provided.~~ The N_2 gas purges the residual gas ~~in~~ from the pipe 9a and the chamber 1 in addition to the branch pipes 9b to 9e.

~~According to~~ Thus, the film forming equipment 101 ~~described above,~~ includes the supply source for supplying at least

~~any~~ one ~~of the~~ alkoxy compound having Si-H bonds ~~and the~~ or siloxane having Si-H bonds and the oxygen-containing gas supply source ~~are provided~~, and also the plasma generating means 2, 3, 7, 8 for plasmanizing the film forming gas ~~are provided~~.

The insulating film containing Si, O, C, H can be formed by the plasma CVD method by using the above plasma CVD equipment. Therefore, as shown in a second embodiment described in the following, it is possible to form ~~the~~ an insulating film that has ~~the~~ a low dielectric constant, has ~~the small amount of~~ a low moisture content, is dense and ~~is~~ has excellent ~~in~~ water resistance. Also, this insulating film has ~~the~~ good adhesiveness to ~~the~~ an organic coating insulating film or to an ~~the~~ inorganic coating insulating film, and ~~has the higher capability for~~ is more effective in preventing the diffusion of copper (Cu).

In particular, the power supplies 7, 8 for supplying ~~the~~ powers ~~having two~~ at high and low frequencies, respectively, to the first and second electrodes 2, 3 ~~of parallel-plate type respectively~~ are connected ~~to them~~. Therefore, the plasma can be generated by applying the powers ~~having these two~~ at high and low frequencies to the electrodes 2, 3 respectively. ~~Thus, the insulating film formed in this manner is dense~~.

Second Embodiment

~~The examination, made by the inventors of the present invention, about the silicon-containing~~

~~insulating film, that is formed by the above plasma CVD equipment, will be explained hereunder.~~

~~First, the well-known~~ Again, conventional parallel-plate type plasma CVD equipment is employed as the ~~above~~ plasma CVD equipment. The lower electrode 3 ~~of the upper and lower electrodes 2, 3~~ is also used as a substrate holder, and the heater 12 for heating the substrate is built into the lower electrode 3.

Formation of Samples

FIGS.2A to 2E are sectional views showing samples having the silicon oxide film (a silicon-containing insulating film) of the present ~~invention~~ embodiment.

As shown in FIG.2A, a sample S1 has a silicon oxide film (this means a silicon-containing insulating film, and referred to as a "PE-CVD TMS SiO_2 film" hereinafter), 42a, ~~that is~~ formed by the PE-CVD method using ~~the~~ a film forming gas containing trimethoxysilane (TMS), on a silicon substrate 41. For the sake of comparison, a comparative sample CS1 ~~having~~ had a silicon oxide film (referred to as a "PE-CVD TEOS SiO_2 film" hereinafter) 51a, ~~that is~~ formed by the PE-CVD method using ~~the~~ a film forming gas containing tetraethoxysilane (TEOS) on the silicon substrate 41, and a comparative sample CS2 ~~having~~ had a silicon oxide film (referred to as a "PE-CVD SiH_4 SiO_2 film" hereinafter) 52a, ~~that is~~ formed by the PE-CVD method using the film forming gas containing monosilane (SiH_4) on the silicon substrate 41. ~~are prepared.~~

As shown in FIG.2E, a sample S1A ~~is~~ was formed by further forming an electrode 45 on the PE-CVD TMS SiO_2 film 42a, of ~~in the~~ sample S1 in which the PE-CVD TMS SiO_2 film 42a is formed on the silicon substrate 41. ~~The~~ A mercury probe is employed as the electrode 45, and ~~a~~ the contact area between the mercury probe and the PE-CVD TMS SiO_2 film 42a ~~is~~ was 0.0230 cm^2.

As shown in FIG.2B, samples S2, S3 ~~are~~ were formed ~~by~~ of ~~forming~~ a BPSG film 43 ~~having an amount of~~ contain~~ed~~ing phosphorus ~~of~~ 7 mol% and having a ~~film~~ thickness of about 500 nm and a PE-CVD TMS SiO_2 film 42b, ~~to be tested~~ in sequence, on the silicon substrate (Si substrate) 41. ~~A film~~ The thickness of the PE-CVD TMS SiO_2 film 42b ~~is set to~~ was 100 nm in the sample S2, and ~~a film~~ the thickness of the PE-CVD TMS SiO_2 film 42b ~~is set to~~ was 200 nm in the sample S3. For comparison, a comparative sample CS3 employ~~ing~~ed a PE-CVD TEOS SiO_2 film 51b having a film thickness of 200 nm in place of the PE-CVD TMS SiO_2 film 42b, a comparative sample CS4 employ~~ing~~ed a PE-CVD SiH_4 SiO_2 film 52b having a film thickness of 200 nm ~~similarly~~, and a comparative sample CS5 employ~~ing~~ed a silicon nitride film (referred to as a "PE-CVD SiN film" hereinafter) 53, that ~~is~~ was formed by the plasma CVD method using the film forming gas containing SiH_4, NH_3 and N_2 ~~similarly to have a film~~ and had a thickness of 200 nm. ~~are prepared.~~

As shown in FIG.2C, samples S4, S5 ~~are formed by forming~~ had low dielectric constant insulating films 44a,

44b and a PE-CVD TMS SiO_2 film 42c formed in sequence on the silicon substrate (Si substrate) 41. An inorganic coating insulating film 44a ~~is~~ was employed as the low dielectric constant insulating film in the sample S4, and an organic coating insulating film 44b ~~is~~ was employed similarly in the sample S5. For comparison, comparative samples CS6, CS7 employ~~ing~~ed a PE-CVD TEOS SiO_2 film 51c in place of the PE-CVD TMS SiO_2 film 42c, ~~are formed~~. The inorganic coating insulating film 44a ~~is~~ was employed as the low dielectric constant insulating film in the comparative sample CS6, and the organic coating insulating film 44b ~~is~~ was employed similarly in the comparative sample CS7.

The inorganic coating insulating film ~~is such an insulating film that is~~ was formed by coating ~~the coating~~ a liquid such as HSQ (product name: manufactured by Dow Corning Co., Ltd.), MSQ (product name), R7 (product name: Hitachi Chemical Co., Ltd.), etc. In the foregoing, a ~~The~~ compound having one carbon or less ~~is distinctively contained as the component compound~~ was used in the coating liquid. The organic coating insulating film ~~is~~ was formed ~~by~~ from a coating of the ~~coating~~ liquid such as FLARE (product name: manufactured by Allied Signal Co., Ltd.), SiLK (product name: manufactured by The Dow Chemical Co.), etc., in which a ~~The~~ compound ~~having~~ two carbons or more is ~~distinctively~~ contained ~~as the component compound~~ in the coating liquid.

As shown in FIG.2D, a sample S6 ~~is~~ was formed ~~by forming~~ of, in sequence, a PE-CVD TMS SiO_2 film (lower protection layer) 42d having a film thickness of about 150 nm, a coating insulating film (main insulating film) 44c having a film thickness of about 200 nm, and a PE-CVD TMS SiO_2 film (upper protection layer) 42e having a film thickness of about 200 nm ~~in sequence~~ on the silicon substrate 41. The coating insulating film 44c ~~is~~ was formed by spin-coating the coating liquid (FOx (product name)), that is produced by dissolving HSQ (Hydrogen silsesquioxane) in~~to~~ the solvent, then baking the coated liquid at the temperatures of 150, 200, and 350 ℃ for one minute in ~~the~~ nitrogen, respectively, and then curing ~~the resultant~~ at the temperature of 400 ℃ for 50 minutes in ~~the~~ nitrogen. ~~For comparison, a~~ A comparative sample CS8 ~~in which~~ had a PE-CVD TEOS SiO_2 film 51d ~~is~~ formed in place of the PE-CVD TMS SiO_2 film 42d as the lower protection layer and a comparative sample CS9 ~~in which~~ had PE-CVD TEOS SiO_2 films 51d, 51e ~~are~~ formed in place of the PE-CVD TMS SiO_2 films 42d, 42e as the upper and lower protection layers, ~~are prepared~~.

The PE-CVD TMS SiO_2 films 42a to 42e of the samples S1 to S6 ~~are~~ were formed by using the above described plasma CVD ~~equipment~~ apparatus under following film forming conditions.

Film forming gas: TMS+N_2O

TMS gas flow rate: 100 sccm

N_2O gas flow rate: 3000 sccm

Gas pressure: 0.7 Torr

Plasmanizing conditions

Power density applied to the upper electrode 2: 0.3 W/cm^2

(frequency 13.56 MHz)

Power density applied to the lower electrode 3: 0.3 W/cm^2

(frequency 380 kHz)

In this film-forming apparatus, these power densities correspond to ~~to the~~ applied ~~powers~~ 750W to the electrodes, respectively.

Substrate temperature: 300 to 400 ℃

Film forming thickness: t nm

The above plasma CVD apparatus 101 was ~~is~~ also employed for forming the PE-CVD TEOS SiO_2 film 51a of the comparative sample CS1, the PE-CVD SiH_4 SiO_2 film 52a of the comparative sample CS2, the PE-CVD TEOS SiO_2 films 51b to 51e of the comparative samples CS3, CS4, CS6 to CS9, and the PE-CVD SiN film 53 of the comparative sample CS5.

Following characteristics of the PE-CVD TMS SiO_2 films 42a to 42e formed as above were ~~are~~ examined.

(i) Basic characteristic

The film forming rate of the above film forming conditions was in ~~is at~~ the range of about 160 to 170 nm/min.

Also, the refractive index of the formed PE-CVD TMS SiO_2 film was in ~~is at~~ the range of 1.477 to 1.48, and the film

stress ~~is~~ was -250 Mpa or 3.0×10^{9} dyne/cm^{2}. ~~The~~ An ellipsometer using ~~the~~ a He-Ne laser having a wavelength of 6338 angstroms ~~is~~ was employed to measure the refractive index. Also, the optilever laser scanning system ~~is~~ was employed to measure the film stress.

Also, the film thickness (t) ~~is~~ was 500 nm, and the relative dielectric constant of the PE-CVD TMS SiO_2 film ~~is~~ was 3.9. The sample C1A ~~is~~ was employed as a sample to examine the relative dielectric constant.

The relative dielectric constant ~~is calculated based on the result that is obtained~~ was determined by superposing a small signal having a frequency of 1 MHz onto the DC voltage (V) applied between the Si substrate 41 and the electrode 45 in the examined sample S1A, and then measuring the change in ~~a~~ capacitance (C) in response to the change in the DC voltage (V).

(ii) Concentration of Carbon and Nitrogen in the film

~~A concentration~~ Concentration of carbon and nitrogen in the PE-CVD TMS SiO_2 film 42a ~~is~~ was measured by the auger electron spectroscopy method (AES method) using the sample S1.

According to the ~~measuring~~ results, the concentration of carbon ~~is~~ was 1.0 ~~atoms~~ atomic%, and the concentration of carbon is 2.1 ~~atoms~~ atomic%.

(iii) Film density

The film density of the PE-CVD TMS SiO_2 film 42a ~~is~~ was examined employing the sample S1 by the well-known

X-ray interference method or weight measuring method.

By way of comparison, similar examination~~s are~~ was carried out ~~to~~ for the thermal SiO_2 film, the comparative sample CS1 of the PE-CVD TEOS SiO_2 film 51a, and the comparative sample CS2 of the PE-CVD SiH_4 SiO_2 film 52a in place of the PE-CVD TMS SiO_2 film 42a.

As shown in FIGS.3A and 3B, it ~~is~~ was found that the PE-CVD TMS SiO_2 film 42a has ~~the high~~ a film density of 2.33, higher ~~rather~~ than other insulating films, and ~~is~~ was dense.

(iv) Amount of contained moisture in the film

~~An~~ The amount of contained moisture in both the film that is obtained immediately after ~~the~~ formation (as deposited) and the film that is left for two weeks in the air ~~is~~ was measured employing the sample S1 by the TDS (Thermal Desorption Mass Spectroscopy) method. This TDS method ~~is the way of heating~~ heats the sample and then measur~~ing~~es the molecules emitted from the sample. For the sake of comparison, ~~the~~ a similar examination ~~is~~ was carried out ~~to~~ for the comparative sample CS1 employing the PE-CVD TEOS SiO_2 film 51a.

~~The~~ Examination ~~is~~ was also carried out ~~by~~ with heating as the sample from ~~the~~ room temperature to 800 ℃ ~~by the~~ using TDS analysis equipment and then quanti~~tating~~fying the amount of moisture extracted from the sample.

FIG.4 is a graph showing the ~~examined~~ results. In FIG.4, ~~an~~ the ordinate denotes the amount of moisture (wt%) represented ~~in~~ on a linear scale and ~~an~~ the abscissa denotes

the temperature (℃) represented ~~in~~ on a linear scale.

According to the measurement executed immediately after ~~the~~ film formation (as deposited), when the temperature is ~~risen~~ raised from ~~the~~ room temperature to 800 ℃, the amount of moisture in the PE-CVD TMS SiO_2 film 42a ~~is~~ was 0.11 wt%, whereas the amount of moisture in the PE-CVD TEOS SiO_2 film 51a ~~is~~ was 0.49 wt%. In addition, according to the measurement executed two weeks later, the amount of moisture in the PE-CVD TMS SiO_2 film 42a ~~is~~ increased merely by +0.2 to 0.3 wt% and thus the amount of moisture ~~is~~ seldom varied.

As described above, it is found that both the structural water (the moisture contained in the film due to the film forming gas and the film structure immediately after the film formation) and the water physical adsor~~ption~~bed ~~water (the incoming moisture that is adsorbed and absorbed physically)~~ in the PE-CVD TMS SiO_2 film 42a ~~are~~ were small in contrast to the PE-CVD TEOS SiO_2 film 51a.

(v) FT-IR Absorption Intensity

~~Then, Examined~~ Results ~~of the~~ for infrared ray~~s~~ absorption intensity in the sample S1 by the FT-IR analysis method (Fourier Transform Infrared analysis method) are shown in FIG.5A. Similarly, ~~examined~~ results ~~in the~~ for comparative samples CS1, CS2 are shown in FIG.5B.

~~An~~ The ordinate of FIG.5A denotes the absorption intensity expressed ~~in~~ on a linear scale (arbitrary unit),

and ~~an~~ the abscissa denotes the wave number expressed ~~in~~ on a linear scale (cm^{-1}). Similarly, this is true of FIG.5B.

As shown in FIG.5A, the peak of the infrared ray~~s~~ absorption intensity, having a center wave number in a range of 2270 to 2350 cm^{-1}, is confirmed. In contrast, as shown in FIG.5B, such a peak is not ~~watched in the~~ seen for comparative samples CS1, CS2.

(vi) Water Resistance

The water resistance of the PE-CVD TMS SiO_2 film 42b ~~is exampled~~ was examined by the high pressure humidifying test (pressure-cooker test) ~~while~~ using the samples S2, S3 shown in FIG.2B. By way of comparison, ~~the~~ a similar examination ~~is~~ was applied to the comparative sample CS3 employing the PE-CVD TEOS SiO_2 film 51b in place of the PE-CVD TMS SiO_2 film 42b and the comparative sample CS5 employing the PE-CVD SiN film 53, ~~similarly~~.

The conditions of the high pressure humidifying test are given as follows. The ~~leaving~~ time of exposure ~~is~~ was used as a parameter.

Temperature: 121 ℃

Pressure: 2.0 atm

Humidity: 100 % R.T. (Room Temperature)

Evaluation of the water resistance ~~is~~ was carried out by evaluating ~~an~~ the amount of P=O bonds contained in the examined insulating film after the high pressure humidifying test. In order to evaluate the amount of P=O bonds contained in the BPSG film 43, the P=O

absorption coefficient ~~is~~ was measured by the FT-IR analysis method. If ~~the~~ moisture enters into the BPSG film 43, the P=O bonds in the film react with the moisture and are ~~to~~ thereby destroyed. In this case, if the PE-CVD TMS SiO_2 film 42b ~~for~~ covering the BPSG film 43 has ~~the~~ high water resistance, such film does not allow pass through the moisture to and thus the P=O bonds in the BPSG film 43 are ~~never~~ not destroyed. As a result, it is possible to say that, ~~if~~ as the time dependent change of the P=O absorption coefficient becomes smaller, the water resistance becomes higher.

FIG.6 is a graph showing the time dependent change of ~~an~~ the amount of contained phosphorus in the insulating film after the high pressure humidifying test is carried out. ~~An~~ The ordinate denotes the P=O absorption coefficient (arbitrary unit) expressed ~~in~~ on a linear scale, and ~~an~~ the abscissa denotes the ~~leaving~~ exposure time (H (hour)) expressed ~~in~~ on a linear scale.

Based on the results shown in FIG.6, it is found that, even after both the samples S2, S3 are left for 150 hours as they are, their P=O absorption coefficients are seldom changed from the initial P=O absorption coefficient, regardless of the magnitude of the thickness of the PE-CVD TMS SiO_2 film 42b, like the PE-CVD SiN film 53 in the comparative sample CS5, i.e., the PE-CVD TMS SiO_2 film 42b has ~~the~~ water resistance equivalent to that of the PE-CVD SiN film 53.

Also, the water resistance ~~is~~ was examined by another high pressure humidifying test ~~while using the examined~~ applied to sample S3 and the comparative samples CS3~~,~~ & CS4.

The conditions of the high pressure humidifying test ~~are~~ were the same as above.

The results are shown in FIG.7. ~~An~~ The ordinate of FIG.7 denotes the water resistance (%) expressed ~~in~~ on a linear scale, and ~~an~~ the abscissa denotes the ~~leaving~~ exposure time (H (hour)) expressed ~~in~~ on a linear scale. ~~The sample S3 and the comparative samples CS3, CS4 are used as a parameter.~~

~~Like the~~ In the manne described above, ~~the~~ evaluation of the water resistance ~~is~~ was carried out by ~~evaluating an~~ determining the amount of P=O bonds contained in the examined insulating film after the high pressure humidifying test. The water resistance in FIG.7 is derived by calculating the P=O absorption coefficient obtained after the high pressure humidifying test on the basis of the P=O absorption coefficient before ~~the leaving-off, that is assumed~~ taken as 100.

As shown in FIG.7, it ~~is~~ was found that the sample S3 ~~has the~~ had water resistance of 97.4 % (100 H), ~~that~~ a value exceed~~s~~ing that of the comparative samples CS3, CS4.

(vii) Leakage current of the film

~~The examined~~ A sample S1A was formed as shown in FIG.2E ~~is formed~~. That is, the electrode 45 ~~is~~ was formed on the PE-CVD TMS SiO_2 film 42 having a film thickness (t) of 200 nm, i.e. on ~~in~~ the

sample S1 according to the present invention.

The leakage current flowing through the silicon substrate 41 and the electrode 45 ~~is~~ was measured by applying ~~the~~ voltage between the silicon substrate 41 and the electrode 45. The silicon substrate 41 ~~is~~ was grounded, and ~~the~~ a negative voltage ~~is~~ was applied to the electrode 45.

According to the results, the leakage current of the PE-CVD TMS SiO_2 film 42a ~~as the single substance is~~ was on the order of 10^{-8} A/cm^2 at ~~the~~ an electric field strength of 5 MV/cm, and the breakdown voltage ~~is~~ was about 10 MV/cm in terms of the electric field.

(viii) Adhesiveness of the film

The adhesiveness between the PE-CVD TMS SiO_2 film 42c according to the present invention and the underlying low dielectric constant insulating film 44a, 44b ~~is~~ was examined ~~employing the~~ for samples S4, S5. Also, ~~the~~ a sample which ~~is~~ was subjected to the surface treatment prior to ~~the~~ film formation and ~~the~~ a sample which ~~is~~ was not subjected to the surface treatment ~~are~~ were prepared, and then examined in ~~the~~ similar fashion ~~examination is carried out~~. The surface treatment was executed prior to the film formation ~~is the treatment for~~ reforming of the surface of the processed film ~~by~~ employing ~~the~~ a plasma of N_2, NH_3, H_2, etc.

By way of comparison, the PE-CVD TEOS SiO_2 film 51c ~~is~~ was employed in place of the PE-CVD TMS SiO_2 film 42c, and similar examinations ~~are~~ were carried out employing the inorganic coating insulating film 44a (the comparative

sample CS6) and the organic coating insulating film 44b (the comparative sample CS7)as the low dielectric constant insulating film.

~~As the test~~ For examining the adhesiveness of the film, ~~the~~ a peel test ~~by~~ using the tape and ~~the~~ a peel test by the CMP (Chemical Mechanical Polishing) ~~on~~ over the entire surface of the wafer ~~are~~ were carried out.

According to the ~~examined~~ results of examination, regardless of the ~~presence~~ use of the surface treatment prior to the film formation, the PE-CVD TMS SiO_2 film 42c ~~has the~~ showed good adhesiveness to the inorganic coating insulating film 44a and the organic coating insulating film 44b. In contrast, ~~a~~ the degree of the adhesiveness of the PE-CVD TEOS SiO_2 film 51c ~~is~~ was inferior to that of the PE-CVD TMS SiO_2 film 42c as a whole ~~. Then, difference in~~ and the adhesiveness ~~appeared in response~~ differed according to whether or not the surface treatment ~~is~~ was applied prior to the film formation. That is, the sample which ~~is~~ was subjected to the surface treatment prior to the film formation had ~~the~~ higher adhesiveness than the sample which ~~is~~ was not subjected to the surface treatment.

(ix) Defect Generating Rate due to Heat Cycle

The defect generat~~ing~~ion ~~rate~~ due to the heat cycle ~~about the~~ for sample S6 and the comparative samples CS8, CS9 ~~is~~ was examined. Respective samples ~~are~~ were sealed in ~~the~~ a package. Test conditions of the heat cycle ~~are given~~ were as follows. The cycle number is used as a parameter.

High temperature (holding time): 150 ℃ (20 minutes)

Low temperature (holding time): -55 ℃ (20 minutes)

Cycle number: 100, 200, 300, 500 ℃

The results are shown in FIG.9. ~~An~~ The ordinate ~~of~~ in FIG.9 denotes the defect generat~~ing rate~~ion (%) expressed ~~in~~ on a linear scale, and ~~an~~ the abscissa denotes the type~~s~~ of ~~the~~ sample. The ~~types of the~~ samples were ~~are the sample~~ S6, and the comparative samples CS8 and CS9, as explained above, in order from the left side. The partition area indicated by a bar graph denotes ~~a~~ the fraction defective ~~at~~ for a particular cycle ~~number~~, i.e. the partition area hatched by lateral lines denotes the fraction defective at 100 ℃, the partition area hatched by vertical lines denotes the fraction defective at 200 ℃, the partition area hatched by oblique lines denotes the fraction def~~ective at~~ 300 ℃, and the white partition area on a black back ground denotes the fraction defective at 500 ℃.

As shown in FIG.9, in ~~the~~ sample S6 employing ~~the~~ a silicon oxide film of the present invention as both the upper protection layer and the lower protection layer ~~the~~ defects were ~~is~~ generated at 300 ℃ or more, but the amount of defects generat~~ing rate is~~ed was about 2 to 3 % even if the defects generat~~ing rates~~ed at 300 ℃ and 500 ℃ are added. In the comparative sample CS8 employing the silicon oxide film 52d of the present invention only as the lower protection

layer ~~out of the upper protection layer and the lower protection layer~~, ~~the~~ defects ~~is~~ were generated almost uniformly from 100 ℃ to 500 ℃, and the defects generat~~ing rate is~~ed were about 25 % in total. In the comparative sample CS9 not employing the silicon oxide film 42d, 42e of the present invention as both ~~the~~ an upper protection layer and ~~the~~ as a lower protection layer, the defects ~~is~~ were generated from 100 ℃ to 500 ℃. In particular, the defects generat~~ing rate~~ed at 300 ℃ and at 500 ℃ ~~are~~ increased, ~~and~~ so that the defects ~~generating~~ generated ~~rate is~~ totaled about 53 %. ~~in total.~~

(x) Examination of the Cu barrier characteristic ~~to the copper (Cu)~~

(a) TDDB (Time Dependent Dielectric Breakdown) test

The TDDB test measures ~~a~~ the time required to come up to the dielectric breakdown when ~~the~~ a voltage is applied to the sample.

The examined sample ~~is~~ was prepared by stacking the PE-CVD TMS SiO_2 film according to the present invention and the Cu film on the Si substrate in sequence. ~~By way of~~ For comparison, a ~~the similar examination is applied to the~~ sample employing the PE-CVD TEOS SiO_2 film in place of the PE-CVD TMS SiO_2 film, and ~~the~~ a sample interposing the TiN film between the Cu film and the PE-CVD TEOS SiO_2 film were utilized.

~~According to the examined~~ The results ~~the~~ showed a breakdown lifetime of 10×10^5 seconds ~~is~~ obtained at ~~the~~ an electric field strength of 8 MV/cm.

In contrast, in the sample employing the PE-CVD TEOS SiO_2 film, ~~the~~ an electric field strength ~~is~~ of 8 MV/cm ~~to get~~ resulted in a ~~the~~ breakdown lifetime on the order of 10×10^5 seconds. This means that the breakdown lifetime of the sample employing the PE-CVD TMS SiO_2 film ~~is~~ was longer by almost six figures than the sample employing the PE-CVD TEOS SiO_2 film.

In the sample interposing the TiN film between the Cu film and the PE-CVD TEOS SiO_2 film, ~~the~~ an electric field strength ~~is~~ of 7.5 MV/cm ~~to get the~~ resulted in a breakdown lifetime on the order of 10×10^5 seconds.

With the above, it is possible to say that the sample employing the PE-CVD TMS SiO_2 film has ~~the~~ a longer breakdown lifetime by almost six figures than that of the sample employing the PE-CVD TEOS SiO_2 film and ~~has the~~ serves as a barrier ~~characteristic~~ to Cu, ~~that is~~ equivalent to or ~~more than~~ exceeding that of the TiN film.

(b) Examination of heat resistance

As shown in FIG.10, ~~the examined~~ a sample ~~is~~ was prepared by stacking the PE-CVD TMS SiO_2 film of 125 nm in thickness according to the present invention and the Cu film on the Si substrate (not shown) ~~to~~ in contact ~~to~~ with each other.

~~The examination is made~~ By measuring the distribution of the Cu concentration ~~distribution state~~ in the PE-CVD TMS SiO_2 film ~~on the basis of the state~~ obtained immediately after the film formation (indicated by a dotted line in FIG.10), after the sample is processed for a predetermined time

4 ~~(three types)~~ i.e., 1 hour (chain double-dashed line), 7 hours (solid line), and 15 hours (dot-dash line)) at a ~~the~~ temperature of 470 ℃.

FIG.10 is a graph showing the ~~examined~~ results. In FIG.10, the ~~an~~ ordinate on the left side denotes ~~a~~ Cu concentration and ~~a~~ Si concentration (cm^{-3}) represented on ~~in~~ a logarithmic scale. The ~~An~~ abscissa denotes ~~a~~ depth (nm) measured from one surface of the PE-CVD TMS SiO_2 film toward the Cu film side and is represented on ~~in~~ a linear scale.

As shown in FIG.10, the distribution ~~is~~ seldom changes ~~changed~~ from that ~~the distribution~~ obtained immediately after the film formation. In other words, it is found that the PE-CVD TMS SiO_2 film has is a ~~the~~ sufficiently good barrier ~~characteristic~~ to ~~the~~ Cu.

In the above, the alkoxy compound (e.g. ~~ex.~~ TMS) having Si-H bonds is employed as the silicon-containing gas in the film forming gas. But a ~~the~~ siloxane having Si-H bonds may be employed.

While ~~Also,~~ N_2O is employed as the oxygen-containing gas in the above, ~~But~~ any gas ~~one~~ selected from the group consisting of oxygen (O_2), nitrogen dioxide (NO_2), carbon monoxide (CO), carbon dioxide (CO_2) and water (H_2O) may be employed.

In addition, if ~~any one selected from the group consisting of~~ hydrogen (H_2) or ~~and~~ nitrogen (N_2) is added to the above film forming gas, the density can be further enhanced.

(Third Embodiment)

Next, a semiconductor device and a method of manufacturing the same according to a third embodiment of the present invention will be explained with reference to FIGS.11A and 11B hereunder.

~~FIG.11B is a sectional view showing a semiconductor device according to a third embodiment of the present invention.~~

As shown in FIG.11B, a ~~the~~ silicon oxide film (the silicon-containing insulating film) 24 according to the present invention is formed on the substrate 20a. ~~In~~ The substrate 20a consists of the underlying insulating film 22 and the wiring 23, both ~~are~~ formed on the base substrate 21. The silicon oxide film 24 covers the wiring~~s~~ 23. In the silicon oxide film 24 according to the present invention, the ~~a~~ peak ~~of an~~ absorption intensity ~~of an~~ infrared ray~~s~~ was ~~is~~ in a range of ~~a~~ wave number 2270 to 2350 cm^{-1}, ~~a~~ film density was ~~is~~ in a range of 2.25 to 2.40 g/cm^3, and ~~a~~ relative dielectric constant was ~~is~~ in a range of 3.3 to 4.3.

In this case, the silicon substrate or the base substrate obtained by forming the wiring~~s~~ and the insulating film on the silicon substrate may be employed as the base substrate 21. A ~~The~~ conductive material such as aluminum, copper, etc. may be employed as the material of the wiring~~s~~ 23.

Thus ~~In this manner~~, the silicon oxide film 24 according to the present invention may be employed as the insulating

film that covers the wiring~~s~~ 23. ~~made of the conductive material such as aluminum, copper, etc.~~

~~According to the semiconductor device of the~~ In a third embodiment, the silicon-containing insulating film 24 according to the present invention is formed in ~~to come into~~ contact with ~~the wirings 23~~ and ~~to~~ covering the wiring~~s~~ 23.

The above described silicon-containing insulating film 24 ~~has qualities such that the insulating film~~ is dense, has ~~is~~ excellent ~~in the~~ water resistance, and contains only a ~~has the~~ small amount of ~~contained~~ moisture ~~in the film~~, which are qualitie equivalent to those of a ~~the~~ silicon nitride film, and also has a ~~the~~ smaller relative dielectric constant than that of a ~~the~~ silicon nitride film. As a result, if the silicon-containing insulating film according to the present invention is employed as the protection layer 24 ~~for~~ covering the wiring~~s~~ 23, etc., ~~the~~ corrosion of the wiring~~s~~ 23 can be prevented by preventing moisture ~~the~~ permeation ~~of the incoming moisture~~, while reducing the parasitic capacitance between the wires of wiring~~s~~ 23.

FIGS.11A and 11B are sectional views illustrating steps in ~~showing~~ the method for manufacturing the semiconductor device according to the third embodiment of the present invention. TMS+N_2O is employed as the film forming gas for the PE-CVD TMS SiO_2 film according to the present invention.

First, as shown in FIG.11A, an underlying insulating ~~film 22 made of the~~ PE-CVD TMS SiO_2 film 22 is formed on the

silicon substrate 21 by the plasma CVD method using TMS+N_2O as the film forming gas.

In order to form the PE-CVD TMS SiO_2 film, first the silicon substrate 21 is loaded into the chamber 1 of the plasma film forming apparatus ~~equipment~~ 101 and held by the substrate holder 3. Then, the silicon substrate 21 is heated to maintain a ~~hold at the~~ temperature of 350 ℃. TMS and the N_2O gas are introduced into the chamber 1 of the plasma film forming apparatus ~~equipment~~ 101 shown in FIG.1 at flow rates of 100 sccm and 3000 sccm, respectively, to hold the pressure at 0.7 Torr. Then, ~~the~~ power of 0.3 W/cm^2 at ~~having~~ a ~~the~~ frequency of 380 kHz is applied to the lower electrode 3 and also a ~~the~~ power of 0.3 W/cm^2 at a ~~having the~~ frequency of 13.56 MHz is applied to the upper electrode 2, thereby converting the ~~Accordingly,~~ TMS and N_2O into a ~~are~~ plasma~~tized~~. A ~~The~~ PE-CVD TMS SiO_2 film 22 of about 200 nm in thickness is formed while holding this condition for a predetermined time. ~~According to the examination,~~ The thus formed PE-CVD TMS SiO_2 film 22 was found to have a ~~had the~~ relative dielectric constant of about 3.9 as ~~that is~~ measured at a ~~the~~ frequency of 1 MHz, and a ~~the~~ leakage current of 10^{-8} A/cm^2 at an ~~the~~ electric field strength of 5 MV/cm.

~~Then, the~~ Wiring (lower wiring) 23 was then ~~is~~ formed on the underlying insulating film 22. Then, as shown in FIG.11B, a ~~the~~ PE-CVD TMS SiO_2 film 24 of about 500 nm in thickness was ~~is~~ formed by the same plasma CVD method ~~that is~~ used to form the above described PE-CVD TMS SiO_2 film 22.

As described above, according to the third embodiment of the present invention, the underlying insulating film 22 is formed on the silicon substrate 21 before the wiring 23 is formed. The PE-CVD TMS SiO_2 film is dense, has ~~the~~ good water resistance, and has a low ~~the small~~ amount of contained moisture in the film. Therefore, the underlying insulating film 22 can prevent ~~the moisture in the underlying insulating film 22 and the incoming~~ moisture from reaching the silicon substrate 21.

Also, since the leakage current between the wiring 23 and the silicon substrate 21 is ~~can be~~ suppressed, the transistors, the capacit~~ances~~ors of the memory elements, etc. are covered with the PE-CVD TMS SiO_2 film ~~in case they are~~ formed on the silicon substrate 21. Therefore, ~~the flowing out~~ leakage of the accumulated charge can be prevented and thus the reliability of the device can be improved.

In addition, since the PE-CVD TMS SiO_2 film 24 is formed after the wiring 23 is covered, ~~the~~ corrosion of the wiring 23 due to ~~the~~ moisture in the film 24 and ~~the incoming~~ ambient moisture can be prevented.

Further, since the PE-CVD TMS SiO_2 film 24 has a ~~the~~ lower relative dielectric constant than that of the silicon nitride film and a ~~the~~ small leakage current, the leakage current between the wires as the wiring~~s~~ is ~~can be~~ suppressed and the parasitic capacitance between the wires ~~wirings~~ can be reduced

both for ~~in the situation that a plurality of wirings are provided~~ wires and for adjacent~~ly or the~~ multi-layered wiring. ~~is formed.~~

Fourth Embodiment

Next, a semiconductor device and a method of manufacturing the same according to a fourth embodiment of the present invention will be explained with reference to FIGS.12A to 12C ~~hereunder~~.

FIG.12C is a sectional view showing a semiconductor device according to a fourth embodiment of the present invention.

As shown in FIG.12C, a ~~the~~ low dielectric constant insulating film 25 such as a ~~the~~ porous insulating film, a ~~the~~ SiOF film, or the like is formed to cover the wiring~~s~~ 23, and then the protection layer 26 made of the silicon oxide film (silicon-containing insulating film) of the present invention is formed on the insulating film 25.

In the silicon oxide film 26 of the present invention, the peak of the infrared ray absorption intensity ~~of the infrared rays~~ is in a ~~the~~ range of ~~a~~ wave number 2270 to 2350 cm^{-1}, the film density is in the range of 2.25 to 2.40 g/cm^3, and the relative dielectric constant is in the range of 3.3 to 4.3.

Thus, the ~~The above~~ silicon oxide film 26 has ~~the~~ qualities which are equivalent to those of a ~~the~~ silicon nitride film. The silicon oxide film 26 has a low ~~the small~~ relative dielectric constant, is dense, has ~~is~~ excellent ~~in the~~ water resistance, and has a lot ~~the small amount of contained~~ moisture content. ~~in the~~

~~film~~. Accordingly, if the silicon-containing insulating film according to the present invention is employed as the protection layer 26 that covers the wiring~~s~~ 23, etc., ~~the~~ corrosion of the wiring~~s~~ 23 can be prevented by preventing the permeation of ~~the incoming~~ moisture, while reducing the parasitic capacitance between the wires as wiring~~s~~ 23.

In particular, if ~~the~~ a porous insulating film having ~~the~~ high hygroscopicity is employed as the insulating film 25 that covers the wiring~~s~~ 23, ~~the incoming~~ ingress of ~~the~~ moisture into the porous insulating film can be prevented and also the increase in the dielectric constant due to ~~the~~ moisture absorption can be prevented.

FIGS.12A to 12C are sectional views showing the method of manufacturing the same according to the fourth embodiment of the present invention. TMS+N_2O is used as the film forming gas.

First, as shown in FIG.12A, like the third embodiment, ~~the~~ a underlying insulating film 22 made of the PE-CVD TMS SiO_2 film is formed on the silicon substrate (base substrate) 21 by the plasma CVD method using TMS+N_2O as the film forming gas. The thus formed PE-CVD TMS SiO_2 film 22 had ~~the~~ a relative dielectric constant of about 3.9 ~~that is~~ measured at ~~the~~ a frequency of 1 MHz, and ~~the~~ had a leakage current of 10^{-8} A/cm^2 ~~at the~~ in an electric field strength of 5 MV/cm.

Then, the wiring (lower wiring) 23 is formed on the

underlying insulating film 22. Next ~~Then~~, as shown in FIG.12B, a porous insulating film 25 having a ~~the~~ low dielectric constant and a ~~the~~ film thickness of about 500 nm is formed by the conventional ~~well-known~~ method to complete ~~These elements constitute~~ a substrate 20b.

Then, as shown in FIG.12C, a protection film 26 i.e. ~~made of the~~ a PE-CVD TMS SiO_2 film ~~and~~ having a ~~the~~ film thickness of about 200 nm, is formed by the plasma CVD method that is used to form the above PE-CVD TMS SiO_2 film 22.

As described above, according to the fourth embodiment, the protection film 26 ~~made of the~~ (PE-CVD TMS SiO_2 film) is formed on the porous insulating film 25 that covers the wiring 23. The PE-CVD TMS SiO_2 film is dense, has ~~the~~ good water resistance, and ~~has~~ the ~~small~~ amount of contained moisture in the film is low.

Therefore, the protection film 26 can prevent ambient ~~the incoming~~ moisture from reaching the wiring 23. Also, the leakage current of the overall interlayer insulating film, including the porous insulating film 25, can be reduced ~~suppressed~~.

Fifth Embodiment

Next, a semiconductor device and a method of manufacturing the same according to a fifth embodiment of the present invention will be explained with reference to FIGS.13A to 13F ~~hereunder~~.

No ¶ → FIGS.13A to 13F are sectional views showing the semiconductor device and the method of manufacturing the

~~same according to the~~ fifth embodiment ~~of the present invention~~. In this ~~case~~, ~~like~~ the third embodiment, $TMS+N_2O$ is used as the film forming gas.

~~FIG.13F is a sectional view showing a semiconductor device according to a fifth embodiment of the present invention.~~

As shown in FIG.13F, in the semiconductor device, an underlying insulating film 32 is formed on a base substrate 31, and ~~a~~ lower wiring 33 is formed thereon. Further, an interlayer insulating film is formed in ~~to~~ contact with and covering ~~to~~ the lower wiring 33 ~~and to cover the lower wiring 33~~. The same base substrate ~~as the base substrate~~ 21 as shown in FIG.11B may be employed as the base substrate 31.

The interlayer insulating film is formed by laminating a lower protection layer 34, formed of the silicon-containing insulating film according to the present invention, a main insulating film 35, and an upper protection layer 36, formed of the silicon-containing insulating film according to the present invention, in sequence from the lower layer. In the silicon-containing insulating film according to the present invention, the ~~a~~ peak of the infrared absorption intensity ~~of the infrared rays~~ is in a range ~~of the~~ wave number of 2270 to 2350 cm^{-1}, ~~a~~ film density is in a range of 2.25 to 2.40 g/cm^3, and ~~a~~ relative dielectric constant is in a range of 3.3 to 4.3.

In this embodiment ~~case~~, the porous insulating film or the SiOF

film, that is the insulating film having ~~the~~ a low dielectric constant, may be employed as the main insulating film 35.

~~Also, a~~ A via hole 37 is formed in the interlayer insulating film ~~over~~ covering the lower wiring 33, and ~~The~~ the lower wiring 33 and the upper wiring 38 are connected ~~via~~ through this via hole 37.

As described above, according to ~~the~~ this fifth embodiment, since the lower protection layer 34 made of the PE-CVD TMS SiO_2 film ~~is formed to~~ covers the lower wiring 33, the corrosion of the lower wiring 33 due to the moisture contained in the lower protection layer 34 and the ~~incoming moisture~~ ambient can be prevented.

Further, the upper and lower protection layers 34, 36 made of the PE-CVD TMS SiO_2 film ~~are formed to put~~ sandwich the main insulating film 35 therebetween.

If the main insulating film 35 is formed of ~~the~~ SiOF ~~film~~, the diffusion of ~~the~~ elemental fluorine (F) ~~element~~ into the outer peripheral portions of the upper and lower protection layers 34, 36 can be prevented.

~~Otherwise,~~ In contrast, if the main insulating film 35 is ~~formed of the~~ a porous insulating film, ~~the~~ hygroscopicity is high and the dielectric constant ~~is~~ readily ~~to~~ varies due to the moisture absorption. However, if the main insulating film 35 is sandwiched ~~by~~ between the upper and lower protection layers 34, 36, the permeation of ~~the incoming~~ ambient moisture into the main insulating film 35 can be ~~suppressed~~ reduced and

thus the dielectric constant of the interlayer insulating film ~~can be~~ is stabilized ~~with~~ at a low value. Also, the leakage current of the overall interlayer insulating film containing the porous insulating film 35 can be suppressed.

~~Furthermore,~~ Because the PE-CVD TMS SiO_2 films 34, 36 ~~has~~ have ~~the small~~ a low relative dielectric constant ~~rather than the silicon nitride film,~~ and ~~has the small~~ low leakage current, ~~Therefore~~, in the case of a plurality of wirings ~~are~~ closely arranged ~~closely~~ or ~~a~~ multi-layered wiring ~~is formed~~, the leakage current between the wirings can be suppressed and also the parasitic capacitance between the wirings can be reduced.

~~In this case,~~ If the underlying insulating film 32 formed on the base substrate 31 is ~~formed of the~~ is a PE-CVD TMS SiO_2 film according to the present invention, the ~~reaching~~ permeation of ~~the~~ moisture ~~in~~ to the underlying insulating film 32 and ~~the incoming moisture~~ to the base substrate 31 can be prevented. ~~Also,~~ If ~~the~~ silicon ~~substrate~~ is employed as the base substrate 31, the leakage current between the lower wiring 33 and the base substrate 31 is reduced. ~~Therefore, in case~~ The transistors, ~~the~~ capacitors of the memory devices, etc. ~~are~~ formed on the silicon substrate, ~~they~~ are covered with the PE-CVD TMS SiO_2 film and, ~~As~~ as a result, ~~the flowing-out~~ leakage of the accumulated charges can be prevented and thus the reliability of the device can be improved.

FIGS.13A to 13F are sectional views illustrating steps in ~~showing~~ the method of manufacturing the semiconductor device according to the fifth embodiment of the present invention. In this ~~case, like~~ fifth embodiment, as in the third embodiment, TMS+N_2O is used as the film forming gas.

FIG.13A is a sectional view showing the state after the wiring is formed. In FIG.13A, ~~a reference~~ 31 denotes a silicon substrate(base substrate); 32, an underlying insulating film; and 33, a wiring (lower wiring). If the wiring 33 is ~~the~~ copper ~~wiring~~, a TaN film serving as ~~the~~ a copper barrier ~~to~~ for the underlying insulating film 22 and a Cu film formed by ~~the~~ sputtering, although not shown, are formed between the underlying insulating film 32 and the wiring (lower wiring) 33 ~~from the bottom~~. These films constitute the substrate 20c.

In this state, as shown in FIG.13B, a barrier insulating film (lower protection layer) 34 ~~made~~ of ~~the~~ PE-CVD TMS SiO_2 ~~film having a film~~ having a thickness of about 50 nm is formed on the wiring 33 by the plasma CVD method using TMS+N_2O.

The barrier insulating film 34 is formed by the same manufacturing method as the underlying insulating film 22 in the third embodiment. Because the ~~The~~ same film forming conditions are employed, their explanation will be omitted herein. ~~According to the examination,~~ The formed barrier insulating film 34 was found to have ~~has the~~ a relative dielectric constant of about 3.9 ~~that is~~ measured at ~~the~~ a

frequency of 1 MHz, and a ~~the~~ leakage current of 10^{-8} A/cm^2 in an ~~at the~~ electric field strength of 5 MV/cm.

Then, as shown in FIG.13C, a porous insulating film 35 having a ~~the~~ low dielectric constant and a ~~the film~~ thickness of about 500 nm is formed by a conventional ~~the well known~~ plasma CVD method. ~~As the method of forming~~ The porous insulating film may be formed as ~~there are the method of forming~~ a multi-layered insulating film by repeating the film formation using ~~by~~ the low pressure thermal CVD method and the film formation by the plasma CVD method, by ~~the method of~~ laminating the organic film and the SiO_2 film alternatively and then removing the organic film ~~by ashing~~ using an ~~the~~ oxygen plasma, etc. ~~for example.~~

Next ~~Then~~, as shown in FIG.13D, a thin and highly dense NSG film (silicon oxide film not containing ~~the~~ impurity), that serves as a protection film (upper protection layer) 36 for the porous insulating film 35 in ~~the~~ ashing and ~~the~~ etching, is formed. If no protection film 36 is formed, the quality of the porous insulating film 35 is altered by the process~~ing~~ gas when ~~the~~ ashing ~~of~~ the photoresist film ~~is executed~~ or when the barrier insulating film 34 under the porous silicon-containing insulating film 35 is etched, and thus there is the possibility that the low dielectric constant characteristic is lost ~~degraded~~. The protection film 36 may be omitted. ~~as the case may be.~~

Then, as shown in FIG.13E, a photoresist film (not

shown) is formed ~~and then~~ with an opening ~~portion is formed~~ in the via-hole forming area ~~of the photoresist film~~ by patterning the photoresist film. Then, ~~first~~ the protection film 36 is etched and removed ~~via~~ through the opening ~~portion~~ in the photoresist film by ~~the~~ reactive ion etching (RIE) using ~~the~~ a plasma~~nized mixed gas containing~~ of CF_4+CHF_3. Then, the porous insulating film 35 is etched and removed ~~by~~ using ~~the~~ a mixed gas containing CF_4+CHF_3 ~~whose composition~~ in a ratio ~~is changed from~~ different than that of the gas used in the etching of the protection film 36. Accordingly, an opening ~~portion~~ is formed to expose the barrier insulating film 34. ~~Then, the ashing of~~ The photoresist film is ~~executed~~ then removed by ashing. ~~At this time,~~ The barrier insulating film 34 has ~~the etching~~ resistance against the etching gas for the porous insulating film 35 and the ashing gas for the photoresist film. As a result, the wiring 33 is not ~~badly~~ adversely affected by the etching gas, etc. The concentration of the mixed gas containing CF_4+CHF_3 may be adjusted by adding Ar+O_2, etc. ~~in addition to etching gas.~~

Then, the barrier insulating film 34 is etched and removed via the opening ~~portion~~ in the protection film 36 and the opening ~~portion~~ in the porous insulating film 35 by ~~the~~ reactive ion etching (RIE) using ~~the~~ a plasma~~nized~~ of a mixed gas containing CF_4+CHF_3, that has the same composition ~~ratio~~ as the gas used in the etching of the above protection film 36. Accordingly, a via hole is

formed to expose the barrier insulating film 34. ~~from its bottom portion. At this time,~~ ~~the~~ The lower wiring 33 is ~~has the etching resistance against~~ protected from the etching gas for the above barrier insulating film 34 and, as ~~As~~ a result, the lower wiring 33 is not badly affected by the etching gas. In this case, ~~a~~ the surface of the lower wiring 33 is oxidized. But such oxide film may be removed by exposing to ~~the~~ a hydrogen plasma diluted with a reducing gas, e.g., an inert gas such as NH_3, argon, nitrogen, or the like after the ashing ~~step~~ of the photoresist film and the etching ~~step~~ of the barrier film are completed.

~~Then,~~ As shown in FIG.13F, a conductor ~~ive film~~ is then filled in the via hole 37. ~~Then,~~ Next, ~~an~~ upper wiring 38 made of copper or aluminum is formed ~~to be~~ and connected to the lower wiring 33 through the via ~~the conductive film.~~ hole 37. If the upper wiring 38 is ~~the~~ copper ~~wiring~~, an underlying conductive film consisting of a barrier metal film, e.g., such as a tantalum nitride (TaN) is provided and a copper film formed by ~~the~~ sputtering ~~method~~ is provided in the via hole 37, and then the conductive film is formed thereon.

With the above, the formation of the upper wiring 38 is completed. The upper wiring 38 is connected to the lower wiring 33 ~~via~~ through the via holes in the protection film 36, the porous insulating film 35, and the barrier insulating film 34.

As described above, according to the fifth embodiment, the lower wiring 33 is covered with the

barrier insulating film 34, i.e. ~~made of~~ the PE-CVD TMS SiO_2 film of ~~to which~~ the present invention. ~~is applied.~~

~~By the way, as indicated by the examined~~ The results obtained in the second embodiment show that the PE-CVD TMS SiO_2 film according to the present invention has ~~the~~ qualities equivalent to those of a ~~the~~ silicon nitride film. The PE-CVD TMS SiO_2 is dense, has ~~is~~ excellent ~~in the~~ water resistance, and has a low ~~the small amount of contained~~ moisture content ~~in the film~~. Accordingly, ~~the~~ corrosion of the lower wiring 33 can be prevented by preventing the permeation of ~~the incoming~~ moisture.

In addition, if the underlying insulating film 32 is formed of the PE-CVD TMS SiO_2 film according to the present invention, all peripheral portions of the lower wiring 33 can be protected by the PE-CVD TMS SiO_2 film. Therefore, ~~the~~ corrosion of the lower wiring 33 is further ~~can be~~ prevented ~~much more~~ by prevent~~ing~~ion of ~~the~~ permeation of ~~the~~ moisture from the ~~all~~ peripheral portions of the lower wiring 33.

Further, upper and lower surfaces of the porous insulating film 35 having the low dielectric constant are protected by the barrier insulating film 34 formed of the PE-CVD TMS SiO_2 film and the protection film 36 formed of the PE-CVD TMS SiO_2 film. Accordingly, ~~the~~ permeation of ~~the incoming~~ moisture into the porous insulating film 35 can be prevented. Therefore, variation in the relative dielectric constant due to ~~the~~

moisture contained in the porous insulating film 35 is ~~can be~~ suppressed.

Furthermore, if ~~the~~ moisture is contained in the porous insulating film 35 as formed ~~from the beginning~~, the out-flow ~~flowing out~~ of such moisture at ~~to~~ the periphery ~~al portions~~ can be prevented and thus ~~the~~ corrosion of the lower wiring 33, etc. can be prevented.

~~Besides,~~ The PE-CVD TMS SiO_2 film has a ~~the quality of the~~ density, that is equivalent to that of a ~~the~~ silicon nitride film, but has a ~~the quality of the~~ smaller relative dielectric constant. ~~that is largely different from the silicon nitride film.~~ Accordingly, if the PE-CVD TMS SiO_2 film is employed as the interlayer insulating film, the smaller relative dielectric constant can be maintained. In particular, if the PE-CVD TMS SiO_2 film is employed as the barrier insulating film and the protection film that respectively protect the upper and lower surfaces of the porous insulating film 35, the smaller relative dielectric constant can be maintained for ~~as~~ the whole ~~overall~~ interlayer insulating film made up of ~~containing~~ all of them.

In the above fifth embodiment, a thermal oxide film formed by heating ~~it~~ in an ~~the~~ oxygen-containing atmosphere to oxidize the silicon substrate 31, an NSG film formed by the CVD method using an ~~the~~ organic silicon-containing gas, a BPSG film (BoroPhosphoSilicate Glass), etc. ~~may be employed as~~ the underlying insulating film 32 may be. But the PE-CVD TMS SiO_2 film which is formed by the plasma

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CVD method according to the present invention may be employed.

Sixth Embodiment

FIGS.14A to 14C are sectional views showing a semiconductor device and a method of manufacturing the same according to a sixth embodiment of the present invention.

~~FIG.14C is a sectional view showing a semiconductor device according to a sixth embodiment of the present invention.~~

~~In this~~ The semiconductor device of this sixth embodiment differs ~~, a difference~~ from the that of fifth embodiment ~~is~~ in that a side wall of the via hole 37 is covered with a PE-CVD TMS SiO_2 film 39a of the present invention and thus the porous insulating film 35 is not exposed from the inner surface of the via hole 37.

In this manner, if a sidewall protection layer 39a ~~made~~ of the PE-CVD TMS SiO_2 film is added to the structure shown in FIG.13F, the porous insulating film 35 can be shielded almost completely ~~perfectly~~ from the ambient atmosphere ~~outside~~ by the PE-CVD TMS SiO_2 film according to the present invention. Therefore, the advantage with regard to protection from ~~about the entering and discharging of the~~ moisture explained in connection with the fifth embodiment ~~can be~~ is further enhanced. ~~much more.~~

In order to form ~~implement~~ the above structure, as shown in FIG.14A, the PE-CVD TMS SiO_2 film 39 to which the present invention is applied is formed on the protection film 36 so as to cover the via hole 37, after the step

shown in FIG.13E. Then, as shown in FIG.14B, the PE-CVD TMS SiO_2 film 39 is etched by ~~the~~ anisotropic etching to leave the PE-CVD TMS SiO_2 film 39a on the sidewall of the via hole 37. Then, as shown in FIG.14C, the upper wiring 38 made of copper or aluminum is formed ~~to be~~ and connected to the lower wiring 33 via the conductive film.

~~With the above,~~ While the present invention is explained above in detail ~~based on the~~ with reference to various embodiments, ~~but~~ the scope of the present invention is not limited to the examples ~~given concretely in~~ of the above embodiments. Variations ~~of~~ in the above embodiments may be ~~contained in~~ made within the scope of the present invention without departing from the gist ~~of the present invention.~~ thereof.

Other Embodiments

For example, as shown in FIG.15, the underlying insulating film 22 or 32 is formed only of the PE-CVD TMS SiO_2 film and is formed directly on the silicon substrate 21 or 31. ~~but the~~ however, an underlying insulating film 22 or 32 having a ~~the~~ multi-layered structure consisting of double layers, ~~that are~~ formed by laminating the BPSG film or the thermal oxide film 61 and the PE-CVD TMS SiO_2 film 62 in sequence from the bottom, ~~or more~~ may be ~~formed~~ utilized. In this case, it is important to arrange the PE-CVD TMS SiO_2 film ~~at~~ as the uppermost layer.

Further, as shown in FIG.16, a single interlayer insulating film 63 is interposed between the lower wiring 33 and the upper wiring 65 ~~may be~~ formed on the substrate

20c. In this case, the interlayer insulating film 63 is made of the silicon-containing insulation film. Moreover, the lower wiring 33 and the upper wiring 65 may be connected via an opening ~~portion~~ 64 penetrating ~~formed to~~ ~~perforate~~ the interlayer insulating film 63.

As described above, according to the present invention, the silicon-containing insulating film is formed on the substrate. In the silicon-containing insulating film according to the present invention, the ~~a~~ peak ~~of the~~ infrared absorption intensity ~~of the infrared rays~~ is in a range of ~~the~~ wave number 2270 to 2350 cm^{-1}, the ~~a~~ film density is in a range of 2.25 to 2.40 g/cm^3, and the ~~a~~ relative dielectric constant is in a range of 3.3 to 4.3.

The silicon-containing insulating film is formed by converting into a plasma, a ~~plasmanizing the~~ film forming gas~~s~~ that contains a ~~consists of~~ gas ~~any one~~ selected from the group consisting of ~~the~~ alkoxy compounds having Si-H bonds and ~~the~~ siloxanes having Si-H bonds and an ~~any one~~ oxygen-containing gas selected from the group consisting of oxygen (O_2), nitrogen monoxide (N_2O), nitrogen dioxide (NO_2), carbon monoxide (CO), carbon dioxide (CO_2), and water (H_2O). ~~to react.~~

It has been ~~According to the~~ experimentally shown that the silicon-containing insulating film in the above range for ~~of the~~ peak of infrared ~~the~~ absorption intensity ~~of the infrared rays~~ and in the above range for ~~of the~~ film density is dense, has a ~~the~~ small relative dielectric constant, and has a low ~~the~~ small amount of contained moisture in the film. ~~And that~~

film ~~formed in the above manner is same.~~

Therefore, if the above silicon-containing insulating film is employed as the insulating film ~~to~~ covering wiring~~s~~ or as the barrier insulating film ~~to~~ sandwiching the low dielectric constant insulating film that constitutes the interlayer insulating film interposed between the upper wiring and the lower wiring, the dielectric constant of the insulating film ~~to~~ covering the wiring~~s~~ or that of the overall interlayer insulating film can be lowered while preventing ~~the~~ corrosion of the wiring and preventing ~~the~~ increase in the leakage current.

ABSTRACT OF THE DISCLOSURE

The present invention relates to a film forming method of forming an interlayer insulating film having a low dielectric constant ~~to~~ for cover~~a~~ing wiring. ~~In construction, an~~ The insulating film ~~for~~ covering ~~a~~ wiring is formed on ~~the~~ a substrate by ~~plasmanizing~~ converting into a plasma and reacting a film forming gas ~~, that consists of any one~~ including a component selected from ~~a~~ the group consisting of alkoxy compounds having Si-H bonds and siloxanes having Si-H bonds and ~~any one~~ an oxygen-containing gas selected from ~~a~~ the group consisting of O_2, N_2O, NO_2, CO, CO_2, and H_2O. ~~to react.~~